PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 29/149, B01J 23/80, C07C 31/125

A1

(11) International Publication Number: WO 96/14280

(43) International Publication Date: 17 May 1996 (17.05.96)

(21) International Application Number: PCT/EP95/04380

(22) International Filing Date: 6 November 1995 (06.11.95)

(30) Priority Data:

08/335,018	7 November 1994 (07.11.94)	US
08/335,021	7 November 1994 (07.11.94)	US
08/335,024	7 November 1994 (07.11.94)	US

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(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS AND CATALYST FOR THE DIRECT HYDROGENATION OF CARBOXYLIC ESTERS

(57) Abstract

A process and catalyst for the direct hydrogenation of carboxylic esters which comprises contacting and reacting one or more esters which hydrogen under predominantly liquid phase hydrogenation conditions in the presence of a catalyst comprising a copper compound, a zinc compound and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof, prepared by calcining these compounds at a temperature in the range of 200 to less than 400 °C.

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PROCESS AND A CATALYST FOR THE DIRECT HYDROGENATION OF CARBOXYLIC ESTERS

This invention relates to a process and catalyst for the direct hydrogenation of carboxylic esters in a predominantly liquid phase using a catalyst comprising a copper compound, a zinc compound, and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof.

The hydrogenation of carboxylic acids and carboxylic esters to alcohols is known in the art, and various methods and catalysts have been suggested for effecting the hydrogenation. A commonly practised method involves the use of a copper-chromite-based hydrogenation catalyst. While copper chromite catalysts are successful and commercially available, the disposal of the spent copper chromite catalyst is a problem since chromium can exist in different oxidation states. Some of these oxidation states are reported to be toxic to humans.

From US-A-5,334,779 catalysts and the use thereof in the hydrogenation of carboxylic esters are known. These catalysts are based on oxides of copper, zinc, and a third element selected from the group consisting of aluminium, magnesium, zirconium and mixtures thereof, and are prepared by calcining a precipitate of the (intermediate) catalyst components at temperatures in the range of 400 to 650 °C. These catalysts are suitable for the hydrogenation of carboxylic acid esters to alcohols. However, hydrogen pressures in the upper part of the pressure range of 68 to 170 bar absolute, e.g., 163 bara, are still required for a reasonable activity. Catalysts having a wider operating window, allowing hydrogenation at lower pressures hence remain desirable.

This invention therefore provides a process and catalyst for the direct hydrogenation of carboxylic esters which comprises contacting and reacting one or more carboxylic esters with hydrogen under predominantly liquid phase hydrogenation conditions in the presence of a catalyst comprising a copper compound, a zinc compound, and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof, prepared by calcining these compounds at a temperature in the range of 200 to less than 400 °C.

The present invention relates to a process for the direct hydrogenation of carboxylic esters to form fatty alcohols. Suitable carboxylic ester comprise (i) detergent range methyl esters, (ii) triglycerides and (iii) wax esters.

As used herein, the term "detergent range methyl esters" refers to compounds, typically C_6 to C_{22} compounds, which have been produced by ester exchange of natural oils, such as coconut oil, rape seed oil, and palm oils. Examples of detergent range methyl esters include methyl decanoate (methyl caprate), methyl dodecanoate (methyl laurate), methyl tetradecanoate (methyl myristate), methyl hexadecanoate (methyl palmitate), methyl octadecanoate (methyl stearate), and methyl octadecenoate (methyl oleate).

As used herein, the term "triglycerides" refers to natural triglycerides, typically C_6 to C_{66} compounds, which occur as oils and fats in plants and animals. Examples of triglycerides which can be used as starting materials in the process of the present invention include natural oils, including genetically engineered oils, such as, for example, palm kernel oil, coconut oil, rape seed oil, tallow, and palm oil, and vegetable oils, such as, for example, soybean oil, safflower oil, canola oil, corn oil, peanut oil.

As used herein, the term "wax esters" refers to compounds, typically C_6 to C_{44} compounds, which have been produced by ester exchange of natural triglycerides. Examples of triglycerides which can be used as raw materials to form wax esters include natural oils, such as coconut oil, rape seed oil, and palm oils, and animal fats, such as lard, tallow and fish oil. Examples of wax esters include decyl decanoate (capryl caprate), dodecyl dodecanoate (lauryl laurate), tetradecyl tetradecanoate (myristyl myristate), hexadecyl hexadecanoate (palmityl palmitate), octadecyl octadecanoate (stearate or isostearate), octadecenyl octadecenoate (oleate, linoleate or linolenate), lauryl myristate, myristyl palmitate, oleyl laurate, and docosyl docosanoate (erucyl erucate).

As used herein, "fatty alcohol" refers to an alcohol, preferably a linear alcohol, containing from about 6 to about 22 carbon atoms, preferably from about 10 carbon atoms to about 22 carbon atoms. Typical fatty alcohols produced by the direct hydrogenation process of the present invention include decanol, dodecanol, tetradecanol, hexadecanol, octadecanol, and the like, and mixtures thereof.

The catalyst of the present invention comprises a mixture of a copper compound, a zinc compound, and at least one compound selected from the group consisting of aluminium, zirconium, magnesium a rare earth and mixtures thereof, prepared by calcining these compounds at a temperature in the range of 200 to less than 400 °C.

It has been found that high purity alcohols can be obtained using a catalyst comprising a copper compound, a zinc compound, and at least one rare earth compound. Such catalyst is therefore preferred.

The metal content of the catalyst is calculated in percent by weight (%wt) as the oxide, based on the total weight of the catalyst. All ratios specified herein are metal atoms unless otherwise noted.

The copper content of the catalyst can vary over a wide range for example, from 10 to 80 %wt. However, for an optimal combination of initial catalyst activity and catalyst stability, a copper content in the range of from 25 to 75 %wt is preferred, especially 30 to 70 %wt.

The zinc content of the catalyst is typically in the range of from 10 to 80 %wt. Preferably, the zinc content of the catalyst is in the range of from 15 to 75 %wt, especially from 20 to 70 %wt. The ratio of zinc to copper in the catalyst is generally in the range of from 1:5 to 5:1, and preferably in the range of from 1:4 to 2:1.

The catalyst additionally comprises at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof.

When a rare earth compound is used, the rare earth content of the catalyst is typically in the range of from 0.1 to 20 %wt. Preferably, the rare earth content of the catalyst is in the range of from 0.2 to 15 %wt, especially from 0.3 to 10 %wt.

As used herein, the terms "rare earth" and "lanthanide" refer to the series of elements with atomic numbers ranging from 57 (lanthanum) through 71 (lutetium). With regard to the rare earth (lanthanide) series, mixed metals are readily available commercially. For purposes of the present invention, the rare earth is selected from the group consisting of praseodymium, neodymium, yttrium, lanthanum, samarium, thorium, cerium and mixtures thereof, with lanthanum being preferred.

When the catalyst contains aluminium and/or zirconium and/or magnesium the aluminium and/or zirconium and/or magnesium total content of the catalyst is typically in the range of from 0.05 to 30 %wt. Preferably, the aluminium and/or zirconium and/or magnesium content of the catalyst is in the range of from 0.4 to 20 %wt, especially from 0.6 to 10 %wt.

In one embodiment, the catalyst comprises copper, zinc and zirconium. In another embodiment, the catalyst comprises, copper, zinc and aluminium. In another embodiment, the catalyst comprises copper, zinc, aluminium and zirconium. In another embodiment, the catalyst comprises, copper, zinc and a rare earth. In another embodiment, the catalyst comprises copper, zinc, magnesium and a rare earth.

Various procedures can be used to prepare the catalysts of the present invention. For example, individual solutions of the metals may be prepared and mixed together followed by the addition of an aqueous alkaline solution. Alternatively, a first aqueous solution comprising a copper or zinc salt and a second solution comprising a soluble base and at least one soluble salt of at least one second metal can be prepared, and these two solutions are then added simultaneously to a vessel containing water. In a preferred embodiment, the catalysts are prepared by co-precipitating from aqueous solution thermally decomposable compounds of copper, zinc, and rare earth and/or aluminium and/or zirconium and/or magnesium, washing the precipitate and calcining the precipitate to give the metal oxides. The catalyst precursor is subjected to a reduction treatment to give the active catalyst.

It is understood that the catalyst is usually handled and stored in the form of its precursor, which indeed is referred to in commerce as the "catalyst", although it is not the catalyst in the strict sense of the agent taking part in chemical reactions such as hydrogenation of carboxylic esters. Reduction of the precursor to the catalyst is normally carried out by the operator of the chemical process. The precursor may be in shapes, e.g., pellets, as required by the user of the catalyst, or may be in its condition before the shaping operation, e.g., as powder or lightly compressed powder.

The initial form in which the copper, zinc and rare earth and/or aluminium and/or zirconium and/or magnesium are employed is the oxide, although compounds which are readily converted to the oxide, e.g., the corresponding metal carbonates, are also suitable initially employed as these are converted to the oxide during pretreatment subsequent to the formation of the initially prepared catalyst composition. Pretreatment of the catalyst in hydrogen and operation of the catalyst in the reaction environment will cause at least partial reduction of some of the metals, such as copper, to lower oxidation states, and it is intended that catalysts with these reduced states will fall within the scope of this invention.

In the method of making the catalyst the reaction conditions for the precipitation should be carefully controlled. The temperature for the precipitation is preferably in the range of from 20 to 100 °C, preferably from 50 to 85 °C, and the pH during the precipitation process is maintained between 5.5 and 7.5, preferably between 6.0 to 7.0 and more preferably, between 6.3 and 6.7.

The precipitating agent may be an alkali metal or an ammonium carbonate solution. The precipitate thus obtained is a mixture of carbonates, basic carbonates, oxides, hydrated oxides and hydroxides. The precipitate is washed, preferably several times with water, aged, reslurried and then dried and calcined, preferably in air at a temperature of from 200 to less than 400 °C, with a temperature of 250 to 350 °C being preferred. It has been established that calcining at a higher temperature yields a catalyst of inferior properties.

The drying is carried out at a temperature sufficient to remove the water. This step is conveniently combined with the calcination by a suitable ramping of the temperature from room temperature slowly through the drying temperature, then up to calcination temperature. The

calcined material is shaped, for example, by pelleting under pressure using alumina as a binder, or graphite as lubricant. The oxide mixture is pretreated in a hydrogen-containing atmosphere prior to use as a catalyst to bring it to its most active state. Pretreatment is accomplished by contacting the catalyst with a stream of hydrogen, or of hydrogen mixed with an inert gas or diluent at a temperature ranging from 100 to 400 °C. Suitable diluent gases for the activating gas mixture include nitrogen, the noble gases and mixtures thereof.

In a preferred embodiment, an aqueous solution of copper, zinc and lanthanum salts is employed. Preferably used are copper nitrate, zinc nitrate, and lanthanum nitrate. A second solution of alkali metal or preferably, ammonium carbonate is prepared. The two solutions are heated to a temperature of 20 to 85 °C and simultaneously metered into the precipitation container at rates such that the pH in the precipitation container is maintained between 5.5 and 7.5. Additional water may be used either initially in the precipitation container or added concurrently with the salt solution and precipitation solution. The resulting precipitate is thoroughly washed, dried, calcined at about 300 °C and activated in hydrogen at temperatures ranging from 100 to 400 °C.

In the process of the present invention, one or more carboxylic esters is contacted and reacted with hydrogen in the presence of the above-described catalyst in a reactor. The reactor may be a trickle bed reactor, fixed bed gas-solid reactor, packed bubble column reactor, continuously stirred tank reactor or a slurry phase reactor. The process may be carried out batchwise or in continuous fashion. The reaction is carried out in a predominantly liquid phase. As used herein, the term "predominantly liquid phase" refers to a reaction in which greater than 50%, and approaching 100% of the

reaction mixture (other than hydrogen) is in the liquid phase.

The reaction temperatures are typically in the range of from 170 to 250 °C, preferably in the range of from 190 to 240 °C, and more preferably in the range of from 205 to 230 °C. With respect to the reaction temperatures, it is important to ensure that the temperature does not 250 °C. At temperatures greater than 250 °C, the paraffin make increases to unacceptable levels. The reaction pressures are typically in the range of from 20.7 to 138 bar gauge (300 to 2000 psig), preferably in the range of from 27.6 to 103 bar g (400 to 1500 psig), and more preferably in the range of from 34.5 to 68.9 bar g (500 to 1000 psig). Operation at these low reaction pressures is possible due to the high activity and selectivity of the catalysts. The molar ratio of hydrogen to methyl carboxylic ester in the process of the present invention is in the range of from 20:1 to 700:1, preferably from 50:1 to 650:1, and more preferably, from 100:1 to 600:1. The process is generally carried out at a weight hourly space velocity (WHSV) in the range of from 0.1 hr^{-1} to 5 hr^{-1}, preferably in the range of from 0.1 hr^{-1} to 3 hr^{-1}. The time period required for reaction will vary according to the temperature used, the molar ratio of hydrogen to carboxylic ester, and the partial pressure of hydrogen.

The products produced by the present process include fatty alcohols, (unreacted) wax esters, glycerol, traces of paraffins and unreacted esters. The products are typically separated by conventional means such as, for example, distillation, extraction, filtration, crystallisation, and the like. The desired fatty alcohol products are then used in various applications, such as, for example, detergents such as laundry powders, laundry liquids, etc. and personal care products such as shampoos, etc.

An advantage of the present process is the conversion, i.e., greater than at least about 80 mole %, and approaching 100%, based on the carboxylic ester, as well as the selectivity to alcohols, i.e., greater than 95 mole %, and approaching 100%. As used herein "selectivity" is understood to refer to the selectivity following separation of wax esters, i.e., myristyl myristate, which are recycled. The process also has advantages in that it produces very pure alcohols with very low levels of paraffins at relatively low hydrogen to feed ratios.

Another advantage of the process is the selectivity to linear alcohols, which is typically approaches 100%. The process also has an advantage in that the process allows for the direct conversion of natural oils into linear alcohols while producing very pure alcohols.

The ranges and limitations provided in the present specification and claims are those which are believed to particularly point out and distinctly claim the present invention. It is, however, understood that other ranges and limitations which perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the present invention as defined by the specification and claims.

The invention is further described with reference to the following examples, which are intended to illustrate certain aspects of the invention, without limiting its broader scope.

Illustrative Embodiments

Catalyst Preparation

Example 1

A solution of mixed nitrates, 96 grams (0.41 mole) of cupric nitrate, 60 grams (0.2 mole) zinc nitrate, 3.3 grams (0.008 mole) lanthanum nitrate in one litre of water was heated to 85 °C and placed in a dish and fun-

nel. In a second funnel was placed a hot 50 °C 1 molar solution of ammonium carbonate of sufficient quantity to provide an excess over the metal nitrates. Two solutions were added simultaneously over a period of about 20 minutes to a vessel containing 1 litre of vigorously stirred distilled water at 65 °C. The rates of addition were adjusted so as to maintain the pH of the mixture at about pH equal to about 6.5. After the addition had been completed the slurry was aged at 85 °C for 20 minutes and then allowed to settle and washed 5 times by decantation and reslurrying before being filtered and dried. The mixed carbonates were then calcined at 300 °C for 4 hours. The resulting oxide material was compressed isostatically at 140 MPa (20,000 lbs) and then crushed and sieved.

Example 2

The catalyst preparation procedure for Example 1 was followed, except that 3.47g (0.008 mole) cerous nitrate was used in place of the lanthanum nitrate.

Example 3

The catalyst preparation procedure for Example 1 was followed, except that 3.00g (0.008 mole) zirconyl nitrate was used in place of the lanthanum nitrate.

Example 4

The catalyst preparation procedure for Example 1 was followed, except that 2.2g (0.009 mole) magnesium nitrate hexahydrate was added to the nitrate salt solution.

Example 5

A Cu/Zn/Zr catalyst was prepared as in Example 3, the catalyst was then mixed with 10% by weight of Catapal D alumina (marketed by Vista Chemical Corporation) and a small amount of acetic acid as a peptising agent. The mixture was mulled, then extruded and calcined as described in Example 1.

Example 6

The catalyst preparation procedure for Example 1 was followed, except that 120g (0.55 moles) copper nitrate was used, and the lanthanum nitrate as replaced with 12.0g (0.3 moles) aluminium nitrate nonahydrate.

Catalyst Testing

The catalytic testing was conducted in a typical laboratory scale reactor. The reactor tube used was constructed of 316 stainless steel and included a thermowell. The tube had an outer diameter of 2.5 cm (1 inch) and an inner diameter of 1.5 cm (0.6 inches). An equal volume of silicon carbide, (60-80 mesh) was mixed with 20.00 g of catalyst and centred in the reactor tube between two beds of enough 20 mesh silicon carbide to fill the reactor. The silicon carbide was used as a diluent. The reactor tube was placed in a four-zone furnace equipped with controlling thermocouples and its fittings were tightened. A multi-point thermocouple was inserted in to the thermowell to allow precise monitoring of the temperatures inside the reactor tube.

The catalyst was reduced by initiating a 10.0 L/Hr flow of approximate 5% hydrogen in nitrogen at a unit pressure of 9.3 bar g (135 psig). The reactor was heated at a rate of 60 °C/Hr to 200 °C. The catalyst was held at 200 °C for 17 hours. While maintaining the same flow rate, the catalyst was next reduced with hydrogen for an additional 8 hours.

After reduction, the unit pressure was raised to the desired pressure, (e.g. 41.4 bar g) by adjusting a back pressure regulator. The hydrogen flow was adjusted to the desired flow rate. The reactor temperature was adjusted to the desired setpoint and the catalyst bed temperatures were allowed to equilibrate before the feed was introduced at the desired feed rate. The feed was stored under nitrogen and, if necessary, heated to a temperature above its melting point before being pumped to the reactor

through heated insulated lines to insure proper flow. Typical operating conditions investigated were; temperatures of 150-260 °C; WHSV of 0.1 to 5 per hour; molar hydrogen to feedstock ratios of between 20:1 and 1000:1; and unit pressures between 13.8 138 bar g (200 and 2000 psig). Samples of the feed and products were analysed by GC, NMR, IR, Mass Spectroscopy and elemental analysis.

The results for hydrogenation of pure methyl tetradecanoate (methyl myristate) are shown in Table 1. The results for hydrogenation of coconut oil, employing the catalyst of Example 4, are shown in Table 2. The results for hydrogenation of pure tetradecyl tetradecanoate (myristyl myristate), employing the catalyst of Example 1, are shown in Table 3.

TABLE 1

Temp. (°C)	H_2:Feed	Conversion (%m)	Alcohol (%m)	Paraffin (%m)	Wax (%m)	Purity (%m)
Example 1*:						
204	125:1	97.3	75.8	0.4	23.8	95.9
221	125:1	99.7	84.8	0.6	14.4	98.8
227	200:1	99.9	86.9	1.0	12.5	98.6
Example 2*:						
204	125:1	99.7	63.4	0.04	36.5	98.4
227	200:1	99.9	86.5	0.7	12.8	99.1
Example 3*:						
205	125:1	99.0	73.9	0.1	26.0	98.4
227	200:1	99.9	87.3	0.8	11.9	98.9
Example 4*:						
205	125:1	99.4	70.7	0.1	28.9	98.5
228	200:1	99.9	90.1	0.9	8.9	99.8
Example 5*:						
204	125:1	99.9	87.0	0.6	12.4	99.3
227	200:1	99.9	93.7	1.4	4.7	98.2

TABLE 1 Cont'd)

Temp. (°C)	H_2:Feed	Conversion (%m)	Alcohol (%m)	Paraffin (%m)	Wax (%m)	Purity (%m)
Example 6*:						
205	125:1	99.9	87.0	0.6	12.4	99.3
222	125:1	99.9	93.7	1.4	4.7	98.2

*WHSV = 0.4, pressure = 41.4 bar gauge (600 psig)

TABLE 2

			Product Yield (%wt)	
Time (hrs.)	Temp. (°C)	H_2:Feed (molar)	C_8-C_{18} Linear Alcohols	Heavy Products
1505-1603	215.6	335:1	87.6	12.4
1627-1653	226.7	335:1	92.9	7.1
1673-1777	226.7	523:1	96.6	3.4
1802-1970	215.6	523:1	89.2	10.8
1994-2428	221.1	523:1	94.9	5.1

TABLE 3

Temperature (°C)	H_2:Feed (molar)	WHSV	Conversion (% m)	Selectivity (% m)
215.6	250:1	0.15	83.0	98.7
	585:1	0.15	95.2	98.7
226.7	250:1	0.151	86.3	97.1
	585:1	0.151	99.3	97.0

As can be seen in Table 1 the present process results in conversions greater than 97 mole % and product purities (of alcohol) greater than 95 mole %. It can also be seen that the product yields of alcohol are greater than 95 mole %, and that the paraffin make is less than 2 mole %. As can be seen in Table 2, the present process results in product yields of linear alcohols which are greater than 85 %wt. As can be seen in Table 3, the present process results in conversions greater than 80 mole% and selectivities greater than 95 mole %. It can also be seen than 95 mole %. It can also be seen that conversion is dependent on H_2:Feed ratio and selectivity is lower at higher temperatures. Both conversion and selectivity approach 100 mole% at suitable conditions.

CLAIMS

1. A hydrogenation catalyst comprising a copper compound, a zinc compound and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof, prepared by calcining these compounds at a temperature in the range of 200 to less than 400 °C.

2. A catalyst as claimed in claim 1, wherein prior to the calcining, these compounds are precipitated at a temperature in the range of 20 to 100 °C and a pH between 5.5 and 7.5.

3. A catalyst as claimed in claims 1 or 2, wherein said catalyst is prepared by calcining these compounds at a temperature in the range of 250 to 350 °C.

4. A catalyst as claimed in any one of claims 1 to 3, wherein said catalyst contains copper in the range of from 10 to 80 percent by weight, calculated as the oxide, based on the total weight of the catalyst.

5. A catalyst as claimed in any one of claims 1 to 4, wherein said catalyst contains zinc in the range of from 10 to 80 percent by weight, calculated as the oxide, based on the total weight of the catalyst.

6. A catalyst as claimed in any one of claims 1 to 5, wherein said catalyst comprises at least one rare earth compound.

7. A catalyst as claimed in claim 6, wherein said catalyst contains a rare earth in the range of from 0.1 to 20 percent by weight, calculated as the oxide, based on the total weight of the catalyst.

8. A process for the direct hydrogenation of carboxylic esters which comprises contacting and reacting one or more esters with hydrogen under predominantly liquid

phase hydrogenation conditions in the presence of a catalyst as claimed in any one of claim 1 to 7.

9. A process as claimed in claim 8, wherein said ester is a detergent range methyl ester, a triglyceride, or a wax ester.

10. A process as claimed in any one of claims 8 or 9, wherein said process is carried out at a temperature in the range of from 170 to 250 °C and a pressure in the range of from 20.7 to 138 bar gauge.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/04380

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C29/149 B01J23/80 C07C31/125

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,42 06 750 (HOECHST AG) 9 September 1993 see claims 1-11; example 1	1-10
Y	US,A,5 334 779 (KUO YEONG-JEN) 2 August 1994 cited in the application	8-10
A	see the whole document	1-7
Y	EP,A,0 434 062 (UNION CARBIDE CHEM PLASTIC) 26 June 1991	8-10
A	see the whole document	1-7
X	EP,A,0 152 314 (INST FRANCAIS DU PETROL) 21 August 1985 see the whole document	1-7

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
7 February 1996	20.03.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Janus, S

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 305 842 (ASAKAWA KAZUO ET AL) 15 December 1981 see the whole document ---	1-7
X	US,A,4 386 017 (NAKAMURA TADASI ET AL) 31 May 1983 see the whole document ---	1-7
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 94-291776 'Catalyst for hydrogenation of furfural to furfuryl alcohol ' & RO,A,106 848 (COMB. CHIM. VICTORIA ET AL) , 30 July 1993 see abstract -----	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 95/04380

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4206750	09-09-93	CA-A- 2090770	05-09-93
		CN-A- 1076438	22-09-93
		EP-A- 0559053	08-09-93
		JP-A- 6009452	18-01-94
US-A-5334779	02-08-94	CA-A- 2162731	08-12-94
		WO-A- 9427721	08-12-94
EP-A-0434062	26-06-91	US-A- 5008235	16-04-91
		AU-B- 625589	16-07-92
		AU-B- 6826490	27-06-91
		CA-A- 2032777	22-06-91
		CN-A,B 1054060	28-08-91
		CN-A- 1105907	02-08-95
		DE-D- 69010170	28-07-94
		DE-T- 69010170	10-11-94
		ES-T- 2055290	16-08-94
		JP-A- 4021638	24-01-92
		KR-B- 9508885	09-08-95
		US-A- 5142067	25-08-92
EP-A-0152314	21-08-85	FR-A- 2558738	02-08-85
		CA-A- 1253132	25-04-89
		JP-A- 60190232	27-09-85
		US-A- 4596782	24-06-86
US-A-4305842	15-12-81	JP-C- 1077821	25-12-81
		JP-A- 55106543	15-08-80
		JP-B- 56021466	19-05-81
		DE-A- 3004514	14-08-80
		FR-A,B 2448385	05-09-80
		GB-A,B 2047556	03-12-80
		NL-A- 8000809	12-08-80
US-A-4386017	31-05-83	JP-C- 1232840	26-09-84
		JP-A- 56070836	13-06-81
		JP-B- 59010256	07-03-84
		DE-A- 3042686	27-05-81
		FR-A- 2469205	22-05-81
		GB-A,B 2064352	17-06-81

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 95/04380

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4386017		NL-A,B,C 8006155	01-06-81

Form PCT/ISA/210 (patent family annex) (July 1992)

· CORRECTED VERSION*

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C07C 29/149, B01J 23/80, C07C 31/125 — **A1**

(11) International Publication Number: **WO 96/14280**

(43) International Publication Date: 17 May 1996 (17.05.96)

(21) International Application Number: PCT/EP95/04380

(22) International Filing Date: 6 November 1995 (06.11.95)

(30) Priority Data:

08/335,018	7 November 1994 (07.11.94)	US
08/335,021	7 November 1994 (07.11.94)	US
08/335,024	7 November 1994 (07.11.94)	US

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(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS AND CATALYST FOR THE DIRECT HYDROGENATION OF CARBOXYLIC ESTERS

(57) Abstract

A process and catalyst for the direct hydrogenation of carboxylic esters which comprises contacting and reacting one or more esters which hydrogen under predominantly liquid phase hydrogenation conditions in the presence of a catalyst comprising a copper compound, a zinc compound and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof, prepared by calcining these compounds at a temperature in the range of 200 to less than 400 °C.

* (Referred to in PCT Gazette No. 22/1997, Section II)

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